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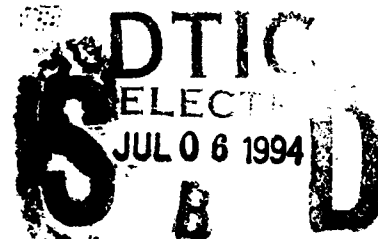
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Rate coefficients and product branching fractions have been determined for 31 ion-molecule reactions involving PF_3 or PF_5^- . About half of the reactions studied show an ion-molecule association channel. NH_2^- and OH^- reaction with PF_5 yields HF product. F^- and electron transfer channels are also observed in many of the reactions studied. Consideration of the efficiency of the electron transfer channel in these reactions leads to the conclusion that the adiabatic electron affinity of PF_5 is 0.75 ± 0.15 eV.

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Negative ion reactions with PF₅ and the electron affinity of PF₅

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Rate coefficients and product branching fractions have been determined for 31 ion-molecule reactions involving PF₅ or PF₅⁻. About half of the reactions studied show an ion-molecule association channel. NH₂⁻ and OH⁻ reaction with PF₅ yields HF product. F⁻ and electron transfer channels are also observed in many of the reactions studied. Consideration of the efficiency of the electron transfer channel in these reactions leads to the conclusion that the adiabatic electron affinity of PF₅ is 0.75±0.15 eV.

1. INTRODUCTION

In recent experiments we have determined^{1,2} (nondissociative) electron attachment rate coefficients for a number of perfluorinated compounds, including PF₅, SF₆, and SF₄. The room-temperature rate coefficient for electron attachment to PF₅ is rather small (3.2×10^{-10} cm³ s⁻¹) corresponding to electron attachment in about 1 in every 1000 collisions, and the rate coefficient shows little variation with temperature in the range studied (300–550 K). The attachment rate constants for PF₅ are orders of magnitude below those for attachment to SF₆ (which are nearly collisional and show little temperature dependence) and SF₄ (which is about 1/10th collisional and also shows little temperature dependence), despite the structural and electronic similarity of these three molecules. In order to understand the energetics of the electron attachment, and possibly provide some information on the dynamics of the process, we have determined the electron affinity of PF₅.

Gutsev³ has recently given the results of calculations on the structure and energetics of the complete series of PF_n neutrals and PF_n⁻ ions ($n = 1-6$). His calculations utilized a Hartree-Fock-Slater approach, with a local spin density approximation (LSDA) for the exchange and correlation contributions to the neutrals and anions, and a higher level of theory which included a nonlocal gradient correction to the exchange potential (LSDA/NL). He calculated the adiabatic electron affinity (EA) of PF₅ to be 0.97 eV at the LSDA level of theory and 1.82 eV at the LSDA/NL level. Both of these values lie above Gutsev *et al.*'s earlier estimate of 0.7 eV,⁴ obtained using the discrete variational X_α method. Gutsev found³ that PF and PF₂ have low adiabatic EAs (0.64 and 0.77 eV, respectively). PF₃ was found to have a negative EA, and the electron affinities of PF₄ and PF₆ were found to be quite high, 3.56 and 7.33 eV, respectively. All these values are at the LSDA/NL level, and are uncorrected for differences in zero-point vibrational energy. Little experimental

data exists with which to compare the calculated EAs: the relatively low EAs for PF and PF₂ and the high EAs for PF₄ and PF₆ are in qualitative agreement with the experimental evidence based on their reactive stabilities, and the negative EA for PF₃ is consistent with the fact that PF₃⁻ has never been observed. No data have been reported on the EA of PF₅.⁵

Gutsev,⁶ and Ziegler and Gutsev,⁷ used the LSDA/NL method to calculate the properties of SF_n and SF_n⁻ ($n = 1-6$) including electron affinities. The EAs of SF, SF₄, and SF₆ are now well-established experimentally, as EA(SF)=2.285±0.006 eV,⁸ EA(SF₄)=1.5±0.2 eV,⁹ and EA(SF₆)=1.05±0.10.¹⁰ By comparison, the calculated values are 2.19,⁷ 2.56,⁷ and 3.44 eV,⁶ respectively. The EAs of SF₃ and SF₅ have not been directly measured, but may be deduced from appearance potentials and measured bond energies; EA(SF₃)~3.8 eV¹¹ and EA(SF₅)~4.2 eV.^{11,12} These experimental estimates may be compared to the calculated⁷ values 1.84 and 4.79 eV, respectively. There is no experimental value for EA(SF₂). Although calculated and experimental EAs are in quite good agreement for SF, the calculated values for SF_{n>1} are rather different. We thus conclude that the LSDA/NL method should not be expected to give EA(PF₅) to better than 1–2 eV.

PF₅ is trigonal bipyramidal (*D*_{3h}),¹³ while ESR work¹⁴ and the calculations of Gutsev³ give the ground configuration of PF₅⁻ to be square pyramidal (*C*_{4v} symmetry), with the PF bonds longer than in the neutral. The vertical electron affinity will be substantially greater than the adiabatic electron affinity as a consequence of the large geometry change between ion and neutral. For this reason, as with the related molecules SF₄ and SF₆, it is unlikely—perhaps impossible—for inherently more accurate photodetachment techniques to be used to measure EA(PF₅). In the SF₄ and SF₆ cases, however, the electron affinities have been reliably determined by charge-transfer reactions (or charge transfer equilibrium).^{9,10} In the present experimental work, we have utilized charge-transfer reactions (or lack thereof) to establish EA(PF₅)=0.75±0.15 eV.

PF₅ gas finds applications in ion implantation and molecular implantation doping of silicon with phosphorous¹⁵ and in intercalation chemistry.¹⁶ PF₅ is an interesting molecule in itself; NMR spectra¹⁷ show five equivalent fluorine

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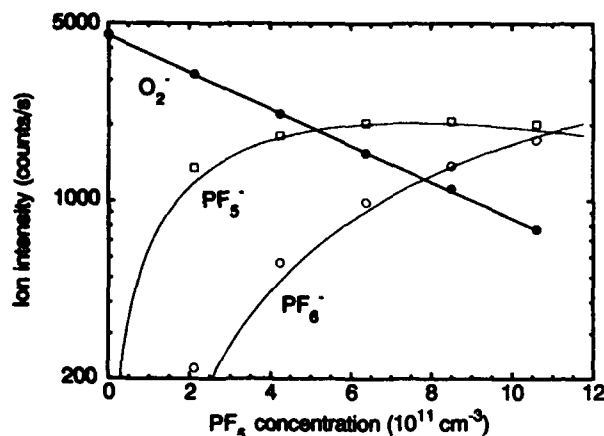


FIG. 1. Analysis of data for O_2^- reaction with PF_5 and the secondary reaction PF_5^- with PF_5 at 300 K. The solid lines were calculated from Eq. (3) with $k_1 = 9.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, $k_2 = 6.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, and a reaction time of 1.7 ms.

atoms while electron diffraction¹³ and IR spectroscopy¹⁸ give axial fluorine bond lengths about 3% longer than equatorial bond lengths. The explanation lies in Berry pseudorotation,¹⁹ large amplitude motions of the F atoms which exchanges F atoms over a time short compared to the NMR time scale. The most recent calculation of the barrier to pseudorotation in PF_5 is that of Marsden,²⁰ who estimated a barrier height of $3.8 \pm 0.5 \text{ kcal mol}^{-1}$. Raman scattering indicates a barrier height between 2.84 and $3.26 \text{ kcal mol}^{-1}$.²¹

II. EXPERIMENT

The measurements were carried out using a selected ion flow tube (SIFT) apparatus. This type of apparatus and associated techniques have been reviewed in detail.^{22,23} Figure 1 shows a sample of the data, for the attenuation of O_2^- intensity as the PF_5 concentration is changed. The logarithmic slope gives a reaction rate coefficient $k = 9.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for this reaction at 300 K.

Anions were produced in an electron-impact ion source as in our work⁹ on SF_4 , supplemented here by $C_6F_5COCH_3^-$ made by electron bombardment from 2',3',4',5',6'-pentafluoroacetophenone vapor; $CF_3C_6H_4CN^-$ from α, α -trifluorotolunitrile vapor; $C_6F_6^-$ from perfluorobenzene vapor; $C_6F_5Cl^-$ from chloropentafluorobenzene vapor; Br^- , $C_6F_5^-$, and $C_6F_4Br^-$ from bromopentafluorobenzene vapor; I^- from iodopentafluorobenzene vapor ($C_6F_5I^-$ could not be made—it dissociated mainly into $C_6F_5^-$ inside the ion source); $C_6F_5CN^-$ from perfluorobenzonitrile vapor; $C_6F_5CF_3^-$ from octafluorotoluene vapor; $C_6F_{11}CF_3^-$ from perfluoromethylcyclohexane vapor; F^- from PF_3 gas; OH^- from water vapor; and NH_2^- from NH_3 gas. The PF_5 gas (Ozark-Mahoning) either contains a small amount of oxide impurity or reacts with oxides deposited on feedline surfaces, as POF_4^- was observed in the mass spectra on both the electron attachment^{1,2} and SIFT apparatuses when PF_5 was the source gas. For use as a reactant neutral, PF_5 was introduced into the flow tube in the form of a 10% mixture in helium gas, pri-

marily because neat PF_5 had a sluggish effect on the flowmeter, but also to allow the flowmeter to be operated closer to full scale (for better control and more accurate flow measurement). The calibration of the reactant flowmeter was checked by timing the pressure drop in a reservoir of known volume connected to the flowmeter inlet.

We were unable to produce PF_5^- in our high-pressure ion source from either PF_5 or PF_3 . Use of a dilute mixture of PF_5/He (<2%) in the ion source led to no significant anion production, while stronger mixtures gave only PF_6^- . Thermal electron attachment to PF_5 is inefficient, but is known¹ to produce PF_5^- , which then fluoride transfers to PF_5 giving the highly stable PF_6^- . Therefore, we were unable to study reverse reactions (i.e., PF_5^- as the reactant) using the standard SIFT technique. Instead, O_2^- was injected into the flow tube, and PF_5^- was generated by efficient charge transfer via reaction (1):



and PF_5^- was then reacted with various neutrals. The secondary reaction



was studied by fitting the PF_5^- and PF_6^- intensities vs PF_5 concentration to solutions of the appropriate rate equations²⁴ as illustrated in Fig. 1. The solid curves in Fig. 1 are given by²⁴

$$I(O_2^-) = I_0 \exp(-k_1 nt), \quad (3a)$$

$$I(PF_5^-) = I_0 [k_1 / (k_2 - k_1)] [\exp(-k_1 nt) - \exp(-k_2 nt)], \quad (3b)$$

$$I(PF_6^-) = I_0 - I(O_2^-) - I(PF_5^-), \quad (3c)$$

where $I(A^-)$ is the detected intensity of ion A^- , I_0 is the initial intensity of O_2^- , k_1 and k_2 are the reaction rate coefficients for reactions (1) and (2), respectively, n is the concentration of PF_5 vapor, and t is the reaction time (reaction distance divided by ion velocity). In fitting Eq. (3) to the data of Fig. 1, it is important that there is little overall loss of ion flux. The reaction was studied with low mass resolution to minimize mass discrimination error; the sum of the O_2^- , PF_5^- , and PF_6^- ion signals was constant to within 3% as n was varied.

Other reactions with PF_5^- reactant proved more difficult to study because yet another neutral reactant must be added. For these other reactions, PF_5 was introduced into the flow tube at an inlet 25 cm ahead of the usual reactant inlets, at a concentration ($4 \times 10^{12} \text{ cm}^{-3}$ at 300 K) sufficient to reduce the O_2^- intensity to less than 1% of the injected current, in a distance of 25 cm. Reactant gases were then added at the usual reactant inlets, and reaction rates were determined from the PF_5^- attenuation. Identification of ionic products was more problematic, however, because of the presence of a large concentration of PF_5 in the flow tube, coupled with secondary processes and the low rate coefficients for several of the reactants studied. Mass spectra were obtained with different concentrations of both PF_5 and the reactant gas (e.g., O_2). In each case it was clear what the major ionic product was, but in some cases it was difficult to say with

TABLE I. Rate coefficients and product branching fractions for reaction of various ions with PF₅ at 300 K. The reactant ions are listed in order of electron binding energy.

Reactant ion	Electron binding energy ^a (eV)	Reaction rate coefficient (10 ⁻¹⁰ cm ³ s ⁻¹)	Calculated reaction efficiency ^b	Ionic products (%)
Fe ⁻	0.151 ±0.003	5.7	0.62	PF ₄ ⁻ (65) FeF ₂ ⁻ (20) FeF ₃ ⁻ (15) PF ₅ ⁻ (100)
O ₂ ⁻	0.451 ±0.007	9.7	0.85	PF ₄ ⁻ (90) PF ₅ ⁻ (10)
C ₆ F ₆ ⁻	0.52 ±0.10	2.5	0.36	PF ₄ ⁻ (90) PF ₅ ⁻ (10)
<i>m</i> -CF ₃ C ₆ H ₄ CN ⁻	0.67 ±0.10	4.1	0.61	PF ₅ ·CF ₃ C ₆ H ₄ CN ⁻ (75) PF ₅ ⁻ (25) PF ₆ ⁻ (<2)
C ₃ F ₃ N ⁻	0.68 ±0.11	2.5 ^c	0.36	PF ₆ ⁻ (80) PF ₅ ⁻ (20)
<i>o</i> -CF ₃ C ₆ H ₄ CN ⁻	0.70 ±0.10	4.0	0.60	PF ₅ ·CF ₃ C ₆ H ₄ CN ⁻ (80) PF ₅ ⁻ (20) PF ₆ ⁻ (<2)
PF ₅ ⁻	0.75 ±0.15	6.2	0.85	PF ₆ ⁻ (100)
<i>p</i> -CF ₃ C ₆ H ₄ CN ⁻	0.76 ±0.10	3.5	0.52	PF ₅ ·CF ₃ C ₆ H ₄ CN ⁻ (85) PF ₅ ⁻ (15) PF ₆ ⁻ (<2)
NH ₂ ⁻	0.771 ±0.005	18.0 ^d	1.2	NPF ₄ ⁻ (70) HNPF ₄ ⁻ (25) HNPF ₅ ⁻ (5)
C ₆ F ₅ Cl ⁻	0.82 ±0.11	4.2	0.64	PF ₅ Cl ⁻ (100)
C ₆ F ₅ CF ₃ ⁻	0.86 ±0.11	1.4	0.22	PF ₆ ⁻ (90) PF ₅ ·C ₆ F ₅ CF ₃ ⁻ (5) PF ₅ ⁻ (5)
C ₆ F ₅ COCH ₃ ⁻	0.88 ±0.11	4.4 ^e	0.67	PF ₅ ·C ₆ F ₅ COCH ₃ ⁻ (100)
SF ₆ ⁻	1.05 ±0.10	3.7	0.52	PF ₆ ⁻ (100)
C ₆ F ₁₁ CF ₃ ⁻	1.06 ±0.10	5.6	0.93	PF ₆ ⁻ (100) ^f
SO ₂ ⁻	1.107 ±0.008	5.4 ^e	0.61	PF ₅ ·SO ₂ ⁻ (100)
C ₆ F ₅ CN ⁻	1.11 ±0.11	1.6	0.25	PF ₅ ·C ₆ F ₅ CN ⁻ (55) PF ₆ ⁻ (45)
C ₆ F ₅ Br ⁻	1.15 ±0.11	≤0.1	≤0.015	PF ₅ Br ⁻ (100)
FeCO ⁻	1.157 ±0.005	4.9	0.60	FeF ₂ ⁻ (75) ^g PF ₄ ⁻ (25)
OH ⁻	1.827 670 ±0.000 021	13.4	0.90	OPF ₄ ⁻ (100)
C ₆ F ₅ ⁻	2.7 ±0.2	5.6	0.83	PF ₅ ·C ₆ F ₅ (100)
I ⁻	3.059 038 ±0.000 010	≤0.05	≤0.007	PF ₅ I ⁻ (100)
Br ⁻	3.363 590 ±0.000 003	0.86	0.10	PF ₅ Br ⁻ (100)
F ⁻	3.401 190 ±0.000 004	15.0 ^e	1.1	PF ₆ ⁻ (100)
Cl ⁻	3.612 69 ±0.000 06	2.5 ^e	0.23	PF ₅ Cl ⁻ (100)
SF ₅ ⁻	3.8 ±0.14	4.7	0.65	PF ₆ ⁻ (100)

^aElectron binding energies (electron affinities of the corresponding neutrals) were taken from Ref. 25, except for PF₅⁻ (this work), SF₅⁻ (Refs. 11 and 12), CF₃C₆H₄CN⁻ (Ref. 26), FeCO⁻ (Ref. 27), C₆F₅⁻ (Ref. 28), and C₆F₁₁CF₃⁻ (Ref. 29).

^bExperimental rate coefficient divided by the calculated collisional rate. The calculation uses the classical trajectory parameterization of Ref. 30 with a PF₅ polarizability of 6.10×10⁻²⁴ cm³ from Ref. 25, and a dipole moment of zero. An efficiency >1 simply reflects uncertainties in the measured and calculated rate coefficients.

^cAlso, 1.7×10⁻¹⁰ cm³ s⁻¹ at 385 K. The product branching fractions were unchanged.

^dCarried out at a center-of-mass kinetic energy of 0.040 eV to enhance signal strengths. The 300 K reaction rate coefficient is likely unaffected by the weak electric field applied.

^eEffective binary rate coefficient measured in a helium buffer at 0.39 Torr (number density 1.25×10¹⁶ cm⁻³). The pressure dependence of the rate coefficient was not studied.

^fFeF₄⁻ also generated, but apparently in a secondary reaction between FeF₂⁻ and PF₅.

^gIt was not possible to inject only C₆F₁₁CF₃⁻ because the ion source mass spectrometer would not reach 350 amu. Instead, all ions produced above about 300 amu were injected; C₆F₁₁CF₃⁻ comprised 90% of the four ions injected. The balance of primary ion loss against ion production implies that PF₆⁻ is the only product from C₆F₁₁CF₃⁻ + PF₅, but this cannot be stated with certainty.

certainly that the product was a direct product of the PF₅⁻ reaction, or to rule out minor products or a PF₆⁻ product. In presenting the results we will refer to these product ions as "terminal" ions. For the PF₅⁻ reaction with O₂, a low (but fixed) PF₅ concentration resulted in residual O₂⁻ surviving the entire length of the flow tube, but, significantly, no increase in the O₂⁻ signal was observed as the concentration of O₂ was increased; only the O₂·PF₅⁻ ion was created in the reaction zone. Only five reactions with PF₅⁻ were studied because of the expense of the PF₅ and the difficulty in pinning down the products; except for the O₂ reaction, these reactions with PF₅⁻ were of no use in bracketing EA(PF₅). Certain reactions that might be of interest (e.g., PF₅⁻ + CF₃C₆H₄CN) from the point of view of determining EA(PF₅), were not studied because of the low vapor pressures of the reactants.

The reaction rate coefficients reported here are estimated to be accurate to ±30%. When more than one product ion is observed in a reaction, the branching ratios are considered to be accurate to within ten percentage points. Neutral products were not detected, but may usually be inferred from the energetics of the reactions.

III. DISCUSSION OF RESULTS

Results of the present measurements for PF₅ reactant are given in Table I. Also given are electron binding energies^{11,12,25-29} of the reference anions and the reaction efficiency (measured rate constant divided by the collisional rate constant). The collisional rate constant was calculated using the method of Su³⁰ which uses the PF₅ polarizability²⁵ of 6.10 × 10⁻²⁴ cm³. Table II gives the present results for PF₅⁻ reactant. In Table III are given the temperature dependences of rate coefficients for reactions (1) and (2) and for the reaction of PF₅⁻ with O₂.

A. Electron transfer channel

Electron transfer to PF₅ was observed in reaction with all anions which have electron binding energies less than 0.76 eV (±0.10 eV), except for Fe⁻. For three anions with electron binding energies in the range 0.77–0.86 eV (±0.10 eV), only the C₆F₅CF₃⁻ reaction showed an electron transfer channel producing PF₅⁻. No anion with an electron binding energy greater than 0.86 eV reacts with PF₅ via electron transfer. Figure 2 displays the electron transfer efficiency (branching fraction times the overall efficiency given in Table I) vs electron binding energy of the reference anion (EA of the corresponding neutral). Three data points in Fig. 2 need special note: those for *o*-, *m*-, and *p*-CF₃C₆H₄CN⁻. These three ions are structurally similar. The partial rate coefficient for the association channel (overall rate coefficient times the association branching fraction) is approximately the same for these three ions (3.0–3.1 × 10⁻¹⁰ cm³ s⁻¹). The decrease in overall rate coefficient (Table I) in going from *m*- to *o*- to *p*-CF₃C₆H₄CN⁻ is entirely due to a decrease in reaction via the electron transfer channel, which may be correlated with the energy available for electron transfer. The data of Fig. 2 imply an upper bound for EA(PF₅) in the neighborhood of 0.9 eV.

TABLE II. Rate coefficients for PF₅⁻ reaction with various molecules at 300 K.

Reactant neutral	Reaction rate coefficient ^a (10 ⁻¹⁰ cm ³ s ⁻¹)	Calculated reaction efficiency ^b	Terminal ionic product ^c
O ₂	0.53	0.091	O ₂ ·PF ₅ ⁻
C ₆ F ₆	3.3	0.38	C ₆ F ₆ ·PF ₅ ⁻
C ₃ F ₃ N	3.1	0.25	C ₃ F ₃ N·PF ₅ ⁻
PF ₅	6.2	0.87	PF ₆ ⁻
C ₆ F ₅ Cl	3.6	0.34	C ₆ F ₅ Cl·PF ₅ ⁻
C ₆ F ₅ CF ₃	10.6	0.80	C ₆ F ₅ CF ₃ ·PF ₅ ⁻

^aEffective binary rate coefficient, measured in a helium buffer at a pressure of 0.4 Torr (He number density 1.25 × 10¹⁶ cm⁻³). The pressure dependence of the reactions was not studied.

^bDefined as in Table I.

^cFor O₂ and PF₅, the product listed is the only ionic product. In the other cases, the ionic product listed is the most intense one observed, and is likely the direct product of reaction. However, because both the reactant neutral and PF₅ were present in the flow tube simultaneously, it is difficult to rule out minor products or a PF₆⁻ product; see the text.

The reaction of PF₅⁻ with O₂ was studied over the temperature range 303–543 K in order to place a lower bound on EA(PF₅); the results are given in Table III. The O₂ reaction was favored over other possibilities listed in Table I because of the clear product picture for the forward reaction, i.e., O₂⁻ reacts only by electron transfer. Despite the experimental difficulties outlined above in regard to identifying products in PF₅ reactions, it was evident that PF₅⁻ does not charge transfer with O₂ even at 543 K. If we take the ratio of the rate coefficient for the PF₅⁻ + O₂ reaction to that for O₂⁻ + PF₅ as an upper limit to an equilibrium constant relating PF₅⁻ and O₂⁻ at 543 K, we obtain a lower limit to [EA(PF₅)–EA(O₂)] of 0.19 eV.³¹ Thus, EA(PF₅) > 0.64 eV.

Combining the considerations above, we assign EA(PF₅) = 0.75 ± 0.15 eV. The uncertainty is slightly larger than implied by the discussion above because of the corresponding uncertainties in the reference EAs, typically ±0.11 eV, except for O₂ [EA(O₂) = 0.451 ± 0.007 eV],³² and the possible influence of internal energy on the electron transfer rates. The measured EA(PF₅) is 1 eV smaller than what is apparently the best calculated value,³ and in fact is in good agreement with a cruder theoretical estimate (0.7 eV, Ref. 4). We assume that this agreement is fortuitous.

TABLE III. Reaction rate coefficients (in units of 10⁻¹⁰ cm³ s⁻¹) as a function of temperature. The estimated uncertainty is ±30% for the first two reactions, and ±40% for the third.

Reaction	303 K	390 K	483 K	543 K
O ₂ ⁻ + PF ₅ → PF ₅ ⁻ + O ₂	9.7	10.6	11.2	12.3
PF ₅ ⁻ + O ₂ → O ₂ ·PF ₅ ⁻	0.53 ^a	0.39 ^a	0.21 ^a	0.12 ^a
PF ₅ ⁻ + PF ₅ → PF ₆ ⁻ + PF ₄	6.2	4.6	3.6	4.0

^aEffective binary rate coefficient measured in a helium buffer at the following pressures (and number densities): 303 K, 0.39 Torr (1.24 × 10¹⁶ cm⁻³); 390 K, 0.44 Torr (1.08 × 10¹⁶ cm⁻³); 483 K, 0.46 Torr (9.3 × 10¹⁵ cm⁻³); and 543 K, 0.49 Torr (8.7 × 10¹⁵ cm⁻³). Pressure dependences were not studied at the various temperatures.

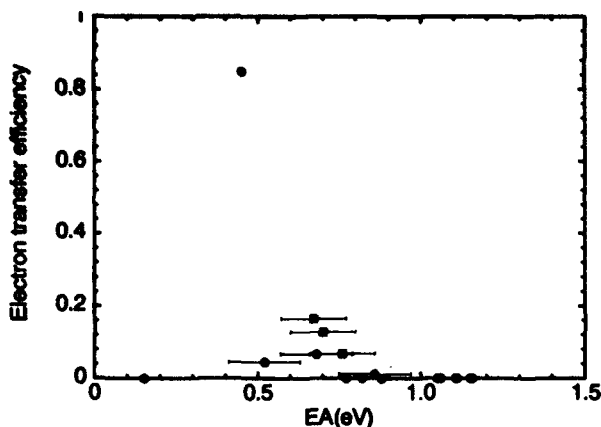


FIG. 2. Efficiency for electron transfer from reference anions to PF₅, vs electron binding energy for the reference anion (electron affinity of the corresponding neutral molecule). The data points labeled ■ are for *m*-, *o*-, and *p*-CF₃C₆H₄CN⁻.

B. Other reaction channels

Fluoride transfer to PF₅ is observed with most of the fluorine-containing anions used in this work. In the cases of *o*-, *m*-, and *p*-CF₃C₆H₄CN⁻, fluoride transfer does not appear to take place, but the secondary reaction of the PF₅⁻ product to yield PF₆⁻ made it difficult to rule out a direct fluoride-transfer channel occurring at the few percent level. Fluoride transfer is generally expected, since according to Larson and McMahon,³³ PF₅ has the largest fluoride affinity known; they estimate it to be 85 ± 10 kcal mol⁻¹ (3.7 ± 0.4 eV). They also showed³³ that chloride affinities of perfluoro compounds are ~0.3–0.5 of the corresponding fluoride affinities. Chloride transfer from C₆F₅Cl⁻ (and Br⁻ transfer from C₆F₅Br⁻) occurs instead of F⁻ transfer, presumably because the halide affinity in the reactant anion is much less than the F⁻ affinity. Association of F⁻, Cl⁻, Br⁻, and I⁻ with PF₅ is observed in the present work; the reaction rate coefficients decrease markedly in the order given, probably indicative of the decreasing halide affinities of PF₅ in the order F⁻, Cl⁻, Br⁻, and I⁻. A similar decrease in efficiency of halide association is seen in their reactions with SF₆.⁹

An association channel was active in about half of the reactions reported here. Indeed, the association channel was generally the main competition faced by the electron transfer channel; without association, our conclusion for EA(PF₅) would be more clear-cut. Association is probably a result of the five-coordinate nature of PF₅, as is the strong fluoride transfer channel that was observed.

It is interesting to contrast the Fe⁻ reaction with PF₅ to the Fe⁻ reactions with SF₄ and SF₆.⁹ In reaction with SF₆, the major product ion observed is F⁻, and charge transfer takes place as a minor channel. In the reaction of Fe⁻ with PF₅, the favored channel is PF₄⁻ + FeF, and simple electron transfer does not take place at all. Comparison may also be made between the FeCO⁻ reactions with SF₆ and PF₅; all yield predominantly FeF_n⁻ products, but PF₅ reactant also produces PF₄⁻ + FeF (25%). The PF₄⁻ ion was also observed by Sullivan and Beauchamp³⁴ and by Larson and McMahon³⁵ in fluoride transfer to PF₅.

Note that the reactions of NH₂⁻ and OH⁻ with PF₅ are characterized by the production of HF, analogous to their reactions with PF₃ and OPF₃.³⁴

IV. CONCLUSIONS

We have determined rate coefficients and product branching fractions for ion–molecule reactions with PF₅ and/or PF₅⁻. Ion–molecule association is observed in about half the reactions studied. Amide and hydroxide reaction with PF₅ result in HF formation. Fluoride transfer and electron transfer channels are also observed in many of the reactions studied. Examination of the energetics of reactions *vis-à-vis* electron transfer leads to the conclusion that the electron affinity of PF₅ is 0.75 ± 0.15 eV.

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